

Kinetics of Hydroformylation of Ethylene in a Homogeneous Medium: Comparison in Organic and Aqueous Systems

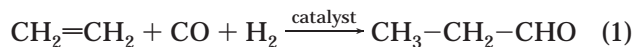
Raj Madhukar Deshpande, Bhalchandra Mahadeo Bhanage, Sunil Sadashiv Divekar, Subbareddiar Kanagasabapathy, and Raghunath Vitthal Chaudhari*

Chemical Engineering Division, National Chemical Laboratory, Pune 411 008, India

The kinetics of hydroformylation of ethylene was studied using $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ and $[\text{Rh}(\text{COD})\text{Cl}]_2/\text{TPPTS}$ catalyst in toluene and water media, respectively. The rates were found to have a first-order dependence on the catalyst concentration. Similar trends were observed with respect to partial pressures of ethylene and carbon monoxide, in both solvents. The difference in the location of the maxima with respect to pressure is due to the poor solubility of the reactants in water as compared to toluene. The major difference observed was a 1.5 order with hydrogen in toluene compared with a first order in water. Rate models were proposed to represent the data observed.

Introduction

Hydroformylation of olefins is an important and largest scale application of homogeneous catalysis in industry, used for the manufacture of C_3 – C_{40} aldehydes and alcohols. Hydroformylation of ethylene is one such example leading to propionaldehyde and *n*-propanol as major products having applications such as solvent, intermediates in the manufacture of pharmaceuticals, pesticides, and perfumery products.



It is also an important step in the new non-HCN route for methyl methacrylate manufacture (Schwaar, 1991). While extensive work has been done on catalysis and product distribution/selectivity in hydroformylation reactions, there is limited published literature on the kinetic modeling of hydroformylation of ethylene. In this paper investigations on the kinetic modeling of hydroformylation of ethylene using a $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ catalyst in an organic medium and a water-soluble Rh/TPPTS (TPPTS = (triphenylphosphine)trisulfonate sodium salt) catalyst in an aqueous medium are reported. The latter case is important from the point of view of separation of products and catalyst, due to the lower solubility of propionaldehyde in aqueous medium. The reaction involves simultaneous absorption of three gases with the catalytic reaction in the liquid phase to produce a single liquid product. A knowledge of the intrinsic kinetics is essential to attempt a systematic analysis of the role of mass transfer in such a system. Such a study not only is useful for the improvement of the catalytic system but also provides the basic information for the design and scale-up of suitable reactors.

The kinetics of hydroformylation of olefins using a homogeneous $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ complex catalyst has been studied by many investigators (Deshpande et al., 1988; Divekar et al., 1993). For hydroformylation of ethylene, however, the available information in the literature is scanty. A few reports describe the kinetics

of this reaction using a supported Rh complex catalyst (Arai et al., 1975; Takahashi et al., 1992). However, on the industrial scale a homogeneous Rh complex is used, and hence it is more important to investigate the kinetics using a soluble Rh complex catalyst. Polievka et al. (1980) have studied the kinetics of hydroformylation of ethylene using homogeneous $\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ but in a very narrow range of conditions. They observed that the rate versus ethylene pressure curve passes through a maximum. The present work deals with the study of the kinetics of hydroformylation of ethylene in an organic medium using a $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ catalyst and in aqueous medium using a $[\text{Rh}(\text{COD})\text{Cl}]_2/\text{TPPTS}$ catalyst and developing rate equations.

In this paper $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ catalyzed hydroformylation of ethylene has been investigated in a temperature range of 333–373 K. The effects of catalyst concentration, partial pressure of CO , H_2 , and ethylene on the rate of reaction have been studied using a stirred pressure reactor. The kinetics of ethylene hydroformylation using a water-soluble $[\text{Rh}(\text{COD})\text{Cl}]_2/\text{TPPTS}$ catalyst has also been investigated at 313 K, wherein the effect of different process parameters on the activity of the catalyst has been observed. The kinetics in these systems have been compared.

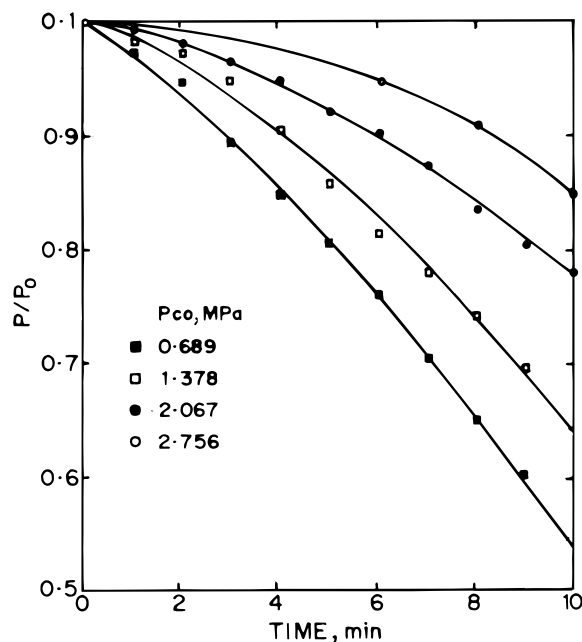
Experimental Section

The reactions were carried out in a stirred batch reactor manufactured by Parr Instrument Co. (Moline, IL), having a capacity of 300 mL. The reactor was connected to a pressure transducer–recorder system for monitoring of the pressure drop in the reactor due to the reaction. The temperature of the reactor was controlled by means of a PID controller and automatic cooling system. The catalyst/ligand was charged along with the solvent into the reactor and heated to the desired temperature. Ethylene was charged individually into the reactor up to the desired pressure until saturation. This was followed by CO and H_2 until the required partial pressure was attained. The whole operation was done at very low agitation speed to ensure that no reaction took place during addition of the reactants. Following this, the agitation was increased

* To whom correspondence should be addressed. Fax: +91 212 333941. E-mail: ihcu@ems.ncl.res.in.

Table 1. Range of Conditions Investigated for the Kinetic Study

description	toluene	water
concentration of catalyst, kmol m ⁻³	(0.5–4.0) × 10 ⁻³	(0.2–1.0) × 10 ⁻³
partial pressure of ethylene, MPa	0.414–2.756	0.414–2.067
partial pressure of hydrogen, MPa	0.414–2.756	0.414–2.067
partial pressure of CO, MPa	0.414–2.756	0.414–2.067
temperature, K	333–373	313
reaction volume, m ³	10 × 4	2.5 × 10 ⁻⁵

**Figure 1.** Typical absorption data for reaction in a toluene medium. Reaction conditions: P_{H_2} , 1.378, MPa; $P_{ethylene}$, 0.689 MPa; concentration of catalyst, 1×10^{-3} kmol m⁻³; temperature, 373 K.

to 900 rpm and the recorder was switched on. The drop in the pressure of the reactor was measured for a fixed time. These data were used to calculate the rates of reaction as follows:

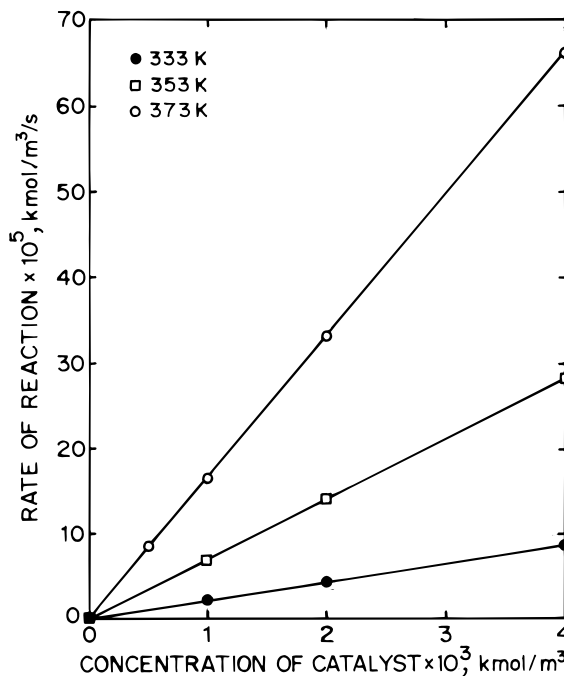
$$R = \frac{[(1 - P/P_0)P_0]V_G}{3ZRTV_L} \quad (2)$$

where V_L = liquid volume in the reactor (m³), V_G = void space in the reactor (m³), Z = compressibility factor; R = gas constant (MPa m³ kmol⁻¹ K⁻¹); T = temperature of the gas in the reactor (K); P = total pressure in the reactor at any time less vapor pressure (MPa), and P_0 = initial pressure in the reactor less vapor pressure (MPa). The rate of reaction is based on the 1:1:1 stoichiometry as shown in eq 1. A typical plot of the pressure drop with time is shown in Figure 1 for the effect of P_{CO} on the rate of reaction at 373 K in toluene. The analysis of the product propionaldehyde was done on GLC using a thermal conductivity detector (TCD). Only hydroformylation products were observed in the reaction crude. No hydrogenation was observed. Hence, the rates calculated by eq 2 were the rates of hydroformylation only.

Using this method the effects of partial pressures of ethylene, CO, and H₂ and catalyst concentration on the rates of reaction in toluene and water were studied in the range of conditions given in Table 1.

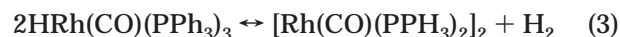
Results and Discussion

(a) Studies in a Toluene Medium Using a HRh(CO)(PPh₃)₃ Catalyst. The effect of agitation speed

**Figure 2.** Effect of catalyst concentration on the rate of reaction in a toluene medium. Reaction conditions: $P_{ethylene}$, 0.689 MPa; P_{CO} , 1.378 MPa; P_{H_2} , 1.378 MPa.

was first investigated at the highest temperature of study (373 K) under standard conditions, and it was observed that the rate was independent of agitation beyond 600 rpm. All reactions were hence conducted at 900 rpm to ensure that the reaction occurs in the kinetic regime. The effect of catalyst concentration on the rate of hydroformylation of ethylene was studied at ethylene, CO, and H₂ partial pressures of 0.689, 1.378, and 1.378 MPa, respectively, in a temperature range of 333–373 K. The results are shown in Figure 2, which indicate a first-order dependence on catalyst concentration. This is expected as enhancement in the catalyst concentration increases the concentration of the active catalytic species and hence the rate.

Effect of the Partial Pressure of Hydrogen. The effect of the partial pressure of hydrogen was studied at ethylene and CO partial pressures of 0.689 and 1.378 MPa, respectively, in a temperature range of 333–373 K and at catalyst concentration of 1.0×10^{-3} kmol/m³. The results are shown in Figure 3. It is observed that the rate has a strong positive dependence on hydrogen pressure of the order of 1.5. Similar trends were earlier reported by Deshpande et al. (1988) for hydroformylation of 1-hexene. At lower P_{H_2} formation of dimeric species is possible as shown by (Evans et al., 1968)



The formation of such species will lead to a reduction in the concentration of active catalytic species which will be more pronounced at lower hydrogen pressures.

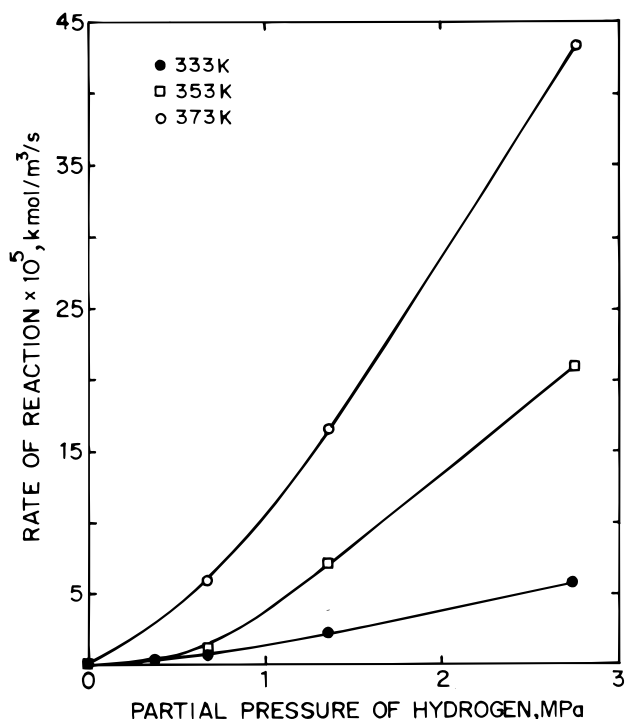


Figure 3. Effect of the partial pressure of hydrogen on the rate of reaction in a toluene medium. Reaction conditions: P_{ethylene} , 0.689, MPa; P_{CO} , 1.378, MPa; concentration of catalyst, 1×10^{-3} , kmol m^{-3} .

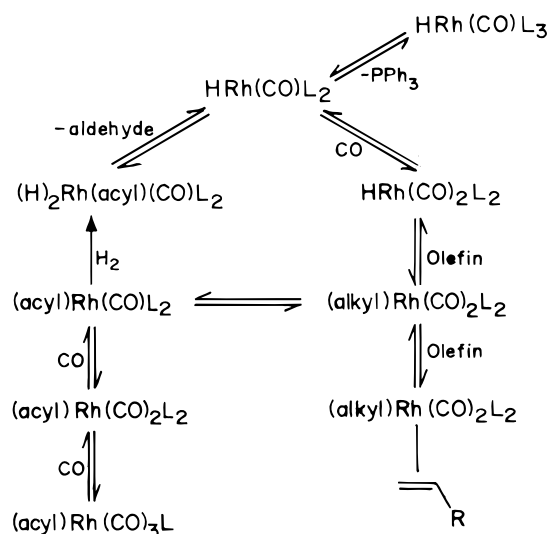


Figure 4. Mechanism of hydroformylation using a $\text{HRh(CO)-(PPh}_3)_3$ catalyst.

Besides this, as shown in Figure 4, the oxidative addition of H_2 to acyl species is the rate-determining step in this reaction. A combined effect of these two steps could give an order of reaction higher than unity.

Effect of the Partial Pressure of Ethylene. The effect of the partial pressure of ethylene was studied at H_2 and CO partial pressures of 1.378 MPa each, in a temperature range of 333–373 K and at a catalyst concentration of 1.0×10^{-3} kmol/m^3 . The results are shown in Figure 5. It is observed that the rate is inversely proportional to the ethylene concentration and shows a typical substrate inhibition. The formation of alkyl olefinic complexes like $\text{C}_2\text{H}_5\text{Rh(CO)}_3\text{C}_2\text{H}_4$ in hydroformylation of ethylene with a $\text{Rh}_4(\text{CO})_{12}$ catalyst has been reported by King et al. (1980). In the present

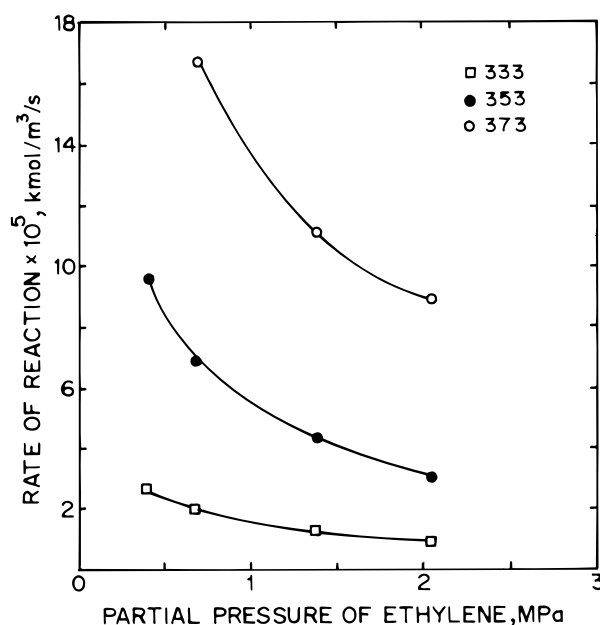


Figure 5. Effect of the partial pressure of ethylene on the rate of reaction in a toluene medium. Reaction conditions: P_{H_2} , 1.378 MPa; P_{CO} , 1.378 MPa; concentration of catalyst, 1×10^{-3} kmol m^{-3} .

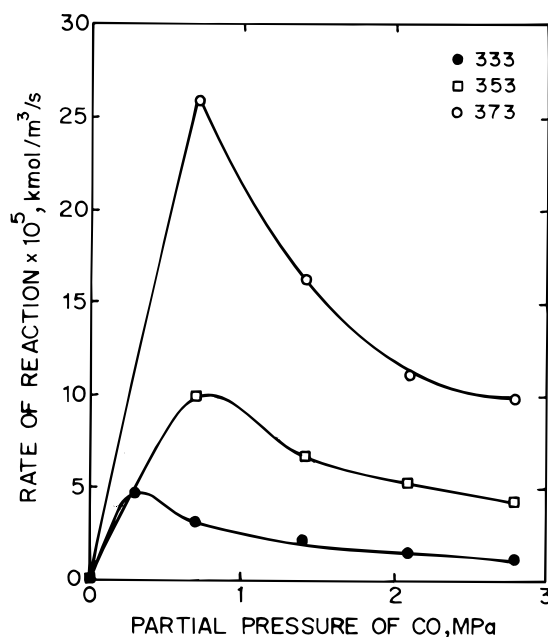


Figure 6. Effect of the partial pressure of CO on the rate of reaction in a toluene medium. Reaction conditions: P_{ethylene} , 0.689 MPa; P_{H_2} , 1.378 MPa; concentration of catalyst, 1×10^{-3} kmol m^{-3} .

work, formation of similar species is possible at high ethylene concentrations, resulting in a lowered concentration of active catalytic species and hence a reduction in the rate of reaction, as seen in Figure 4.

Effect of the Partial Pressure of Carbon Monoxide. The effect of the partial pressure of carbon monoxide was studied at ethylene and H_2 partial pressures of 0.689 and 1.378 MPa, respectively, in a temperature range of 333–373 K and at a catalyst concentration of 1.0×10^{-3} kmol/m^3 . The results shown in Figure 6 indicate a case of a typical substrate-inhibited kinetics which is very well established in hydroformylation reactions. This trend is observed

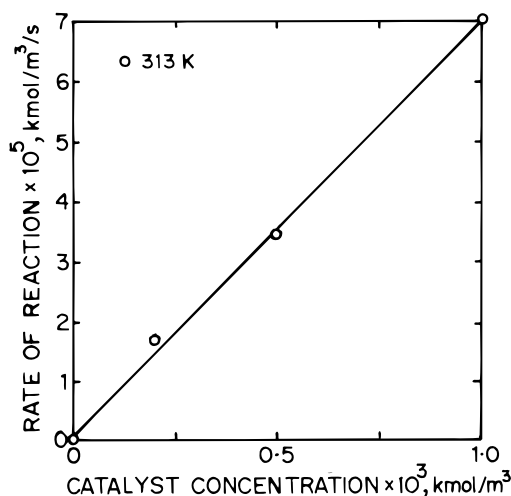


Figure 7. Effect of the catalyst concentration on the rate of reaction in an aqueous medium. Reaction conditions: P_{ethylene} , 0.689 MPa; P_{CO} , 0.689 MPa; P_{H_2} , 0.689 MPa; temperature, 313 K.

since, at high P_{CO} , inactive di- and tricarbonylacylrhodium species are formed, leading to a sharp drop in activity. At lower P_{CO} a positive dependence is observed, pertaining to enhanced formation of active catalytic species $\text{HRh}(\text{CO})_2(\text{PPh}_3)_2$ (Figure 4).

(b) Reactions in an Aqueous Medium Using a $[\text{Rh}(\text{COD})\text{Cl}]_2/\text{TPPTS}$ Catalyst System. The kinetics of hydroformylation of ethylene was also studied using a $[\text{Rh}(\text{COD})\text{Cl}]_2/\text{TPPTS}$ catalyst system. The active catalyst here is analogous to that in a toluene medium. The main objective of this study was to investigate and compare the hydroformylation kinetics in toluene and in a reactive medium like water. This is important since water-soluble catalyst is being commercially applied for hydroformylation of propylene to *n*-butyraldehyde by Hoechst (Cornils and Wiebus, 1995, 1996). The effects of catalyst concentration and partial pressures of ethylene, CO, and H_2 on the rate of reaction were studied at a temperature of 313 K and 1000 rpm (to ensure a kinetic regime).

It may be noted that the catalyst concentration used in this case is half that used in the case of toluene mainly because the reaction was found to be mass transfer controlled at a catalyst concentration of 1×10^{-3} kmol/m³; also, the pressures of CO, ethylene, and hydrogen used for this study are 0.689 MPa each. The catalyst was prepared in situ using $[\text{RhCl}(\text{COD})]_2$ and TPPTS in the ratio of 1:6.

The main objective was also to establish the trends in an aqueous medium and compare with those in an organic medium. Hence, the data were observed at a single temperature of 313 K.

A first-order dependence is observed with respect to the catalyst concentration as shown in Figure 7. This trend is similar to that observed in the case of toluene as the reaction medium. The effect of the partial pressure of hydrogen also shows a first-order dependence (see Figure 8). This result is markedly different from the 1.5 order observed in toluene. Water being a polar solvent, the formation of dimeric species (eq 3) is not facilitated. Besides, the formation of such species will also depend on the concentrations of other reactants like CO and ethylene. It is well-known that the solubilities of all three of these gases are much lower in water as compared to toluene (see Table 2).

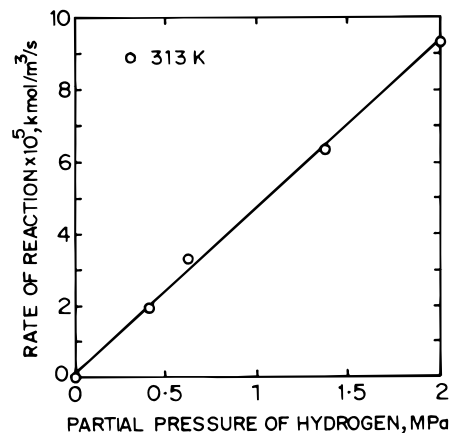


Figure 8. Effect of the partial pressure of hydrogen on the rate of reaction in an aqueous medium. Reaction conditions: P_{ethylene} , 0.689 MPa; P_{CO} , 0.689 MPa; concentration of catalyst, 5×10^{-4} kmol m⁻³; Rh/TPPTS, 1:6; temperature, 313 K.

Table 2. Solubility of Ethylene, CO, and H_2 in Toluene and Water

solvent	temperature, K	solubility, MPa m ³ kmol ⁻¹		
		ethylene	hydrogen	CO
water	313	40.33	191.06	211.04
toluene	333	1.904	61.69	18.51
toluene	353	2.791	90.69	23.02
toluene	373	9.209	153.02	29.62

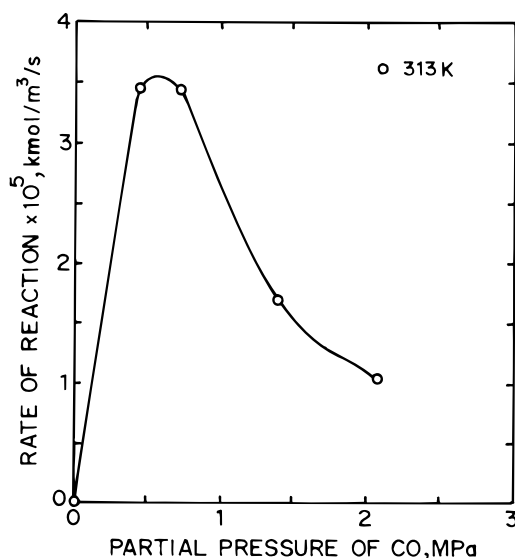


Figure 9. Effect of the partial pressure of CO on the rate of reaction in an aqueous medium. Reaction conditions: P_{ethylene} , 0.689 MPa; P_{H_2} , 0.689 MPa; concentration of catalyst, 5×10^{-4} kmol m⁻³; Rh/TPPTS, 1:6; temperature: 313 K.

The rate versus CO partial pressure passes through a maximum as shown in Figure 9. In contrast, in a toluene solvent, only a negative order dependence is observed with P_{CO} , in the same pressure range (0.4–2.76 MPa). Although, the maxima with P_{CO} have been well documented in hydroformylation chemistry, the difference in the trends observed in water versus those in toluene is due to the poor solubility of carbon monoxide in water as compared to that in toluene. The concentration of CO at low pressures is too low to give the formation of di- and tricarbonylacylrhodium species (see Figure 4), giving a positive order dependence with respect to CO in this range. The inhibition observed at

Table 3. Models Examined To Fit the Data on Ethylene Hydroformylation

model	rate model	<i>T</i> , K	$K_B \times 10^{-2}$	K_E	<i>k</i>	ϕ_{\min}^a
1	$k(A^*)^{1.5}B^*E^*$	333	1.116	15.01	8.202×10^2	3.95×10^{-11}
	$(1 + K_B B^*)^2(1 + K_E E^*)$	353	1.268	23.97	8.873×10^3	2.12×10^{-10}
		373	1.490	26.74	3.007×10^4	1.00×10^{-9}
2	$k(A^*)B^*E^*$	333	1.000	26.47	2.920×10^2	2.350×10^{-10}
	$(1 + K_B B^*)^2(1 + K_E E^*)^2$	353	1.530	28.56	2.208×10^3	3.904×10^{-9}
		373	1.820	58.84	1.520×10^4	7.140×10^{-9}
3	$k(A^*)^{1.5}B^*E^*$	333	0.944	27.69	1.490×10^2	3.830×10^{-10}
	$(1 + K_B B^*)^2(1 + K_E E^*)$	353	1.290	48.86	2.410×10^3	3.790×10^{-9}
		373	1.780	43.45	1.704×10^4	2.350×10^{-8}
4	$k(A^*)^{1.5}B^*E^*$	333	1.380	26.50	2.640×10^2	1.430×10^{-9}
	$(1 + K_B B^*)(1 + K_E E^*)^2$	353	1.010	47.71	2.830×10^3	3.180×10^{-9}
		373	0.153	27.99	4.718×10^3	8.180×10^{-6}
5	$k(A^*)^{1.5}B^*E^*$	333	0.413	20.10	9.410×10^2	7.720×10^{-11}
	$(1 + K_B B^*)^3(1 + K_E E^*)$	353	0.375	-48.61	9.780×10^3	2.020×10^{-9}
		373	0.009	42.20	2.880×10^3	2.210×10^{-8}
6	$k(A^*)^{1.5}B^*E^*$	333	0.924	16.98	5.630×10^2	1.260×10^{-9}
	$(1 + K_B B^*)^3(1 + K_E E^*)$	353	1.268	23.97	8.870×10^3	1.090×10^{-8}
		373	0.023	645.79	2.190×10^4	2.020×10^{-8}

^a ϕ_{\min} is minimized sum of the squares of the difference between observed and predicted rates.

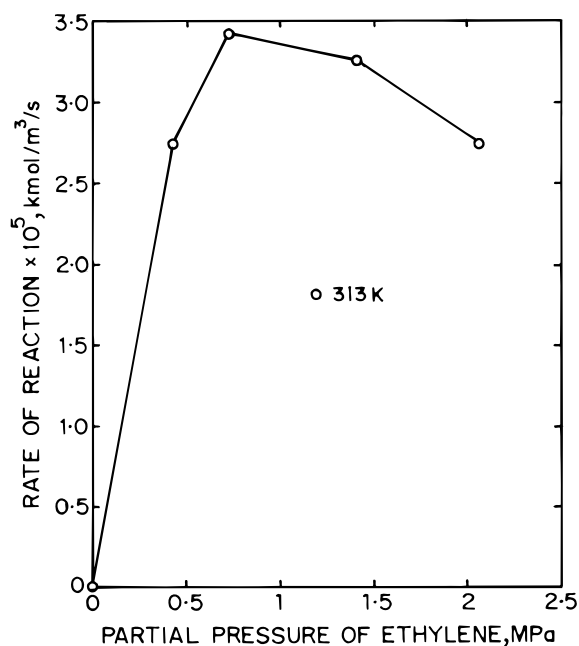


Figure 10. Effect of the partial pressure of ethylene on the rate of reaction in an aqueous medium. Reaction conditions: P_{H_2} , 0.689 MPa; P_{CO} , 0.689 MPa; concentration of catalyst, 5×10^{-4} kmol m^{-3} ; Rh/TPPTS, 1:6; temperature, 313 K.

higher pressures is mainly due to the formation of these inactive species.

Figure 10 shows the effect of the partial pressure of ethylene on the rate of reaction. The trend is similar to that observed with carbon monoxide. A first-order dependence is observed up to an ethylene pressure of almost 1 MPa, whereas in the case of toluene even at a pressure of 0.4 MPa, a negative order is observed. The inhibition with an increase in the ethylene partial pressure is mainly due to the formation of diolefinic species, as mentioned earlier. At lower ethylene partial pressure, in an aqueous medium, the concentration of ethylene is too low to generate inhibitory species and, hence, a first-order dependence is observed. This can be attributed to the increased formation of active alkyl rhodium species (Figure 4) and, hence, rate.

Kinetic Model. In order to ensure that the data observed are in the kinetic regime, the rates were compared with the maximum rates of mass transfer possible under reaction conditions ($k_L a A^*$). For this

purpose, the value of $k_L a$ was obtained as discussed in the literature, for stirred dead-end reactors of the same type as used in this work (Chaudhari et al., 1987). The $k_L a$ was found to be $0.1 s^{-1}$. The solubilities of ethylene, CO, and H_2 in toluene and water were measured using a pressure absorption method, and the values are given in Table 2. The values of α_1 , α_2 , and α_3 as defined by Chaudhari and Doraiswamy (1974) were calculated.

$$\alpha_1 = \frac{R}{k_L a A^*} \quad (4)$$

$$\alpha_2 = \frac{R}{k_L a B^*} \quad (5)$$

$$\alpha_3 = \frac{R}{k_L a E^*} \quad (6)$$

These were found to be less than 0.12, even for the highest rates observed. This confirms the absence of mass-transfer limitations and, hence, the kinetic regime. For the purpose of kinetic modeling the data at constant catalyst concentration were used in either case.

A number of empirical models were examined to represent the observed data. The best model was selected on the basis of the criteria of least average error between the predicted and experimental rates (ϕ_{\min}) defined as

$$\phi_{\min} = \sum_{i=1}^n (R_{\text{pred}} - R_{\text{obs}})^2 \quad (7)$$

and the results are presented in Table 3 for the studies in toluene medium. The values of the constants were evaluated using an optimization routine (Marquardt method). For this purpose initial guess values were obtained by the graphical fitting of the rate data to the respective models. These values were used as the starting values for the optimization program.

The model 5 could not be considered because it gives a negative value for parameter K_E . Also the trend with k is not according to that dictated by thermodynamics. Similarly models 3, 4, and 6 have inconsistent trends in the parameters K_B and K_E and hence were not considered. Between the models 1 and 2, the ϕ_{\min} values were higher for model 2.

The model chosen on the basis of ϕ_{\min} was

$$R = \frac{kA^{*1.5}B^*E^*}{(1 + K_B B^*)^2(1 + K_E E^*)^2} \quad (8)$$

This model was found to predict the rate data within an error of $\pm 8\%$, which is within the range of experimental error. This was found to be in excellent agreement with the predicted rates, as is clear from the low ϕ_{\min} value. The values of k , K_B , and K_E were evaluated for all three temperatures and are given in Table 3. The activation energy was calculated as 9.4×10^4 kJ/kmol.

A similar exercise was undertaken for arriving at a rate model for reaction in an aqueous medium. The rate data obtained were found to be well represented by the following form of rate equation.

$$R = \frac{34550A^*B^*E^*}{(1 + 278B^*)^2(1 + 3829E^*)^2} \quad (9)$$

In this case the model similar to model 2 (Table 3) was found to best fit the observed rate data. A model similar to model 1 (1.5 order with respect to A^*) could not predict the rate particularly for hydrogen dependence.

Conclusions

The kinetics of hydroformylation of ethylene was studied in toluene and water media using $\text{HRh}(\text{CO})\text{-(PPh}_3)_3$ and $[\text{Rh}(\text{COD})\text{Cl}]_2/\text{TPPTS}$ catalyst, respectively. The rates were found to have a first-order dependence with respect to catalyst concentration. Similar trends were observed with respect to the partial pressure of ethylene and carbon monoxide, in both solvents. The difference in the location of the maxima was attributed to the poor solubility of the reactants in water as compared to toluene. The major difference observed was a 1.5 order with hydrogen in toluene versus a first order in water.

The following rate model were found to represent the data in toluene at 333–373 K:

$$R = \frac{kA^{*1.5}B^*E^*}{(1 + K_B B^*)^2(1 + K_E E^*)^2}$$

The following rate model represented the data in an aqueous system at 313 K:

$$R = \frac{34550A^*B^*E^*}{(1 + 278B^*)^2(1 + 3829E^*)^2}$$

within 8% error.

Nomenclature

A^* = concentration of H_2 in toluene or water at a gas–liquid interface, kmol/ m^3

B^* = concentration of CO in toluene or water at a gas–liquid interface, kmol/ m^3

E^* = concentration of ethylene in toluene or water at a gas–liquid interface, kmol/ m^3

k = reaction rate constant in eq 8, $\text{m}^{7.5} \text{kmol}^{-2.5} \text{s}^{-1}$

K_B = constant in eq 8, $\text{m}^3 \text{kmol}^{-1}$

K_E = constant in eq 8, $\text{m}^3 \text{kmol}^{-1}$

P = total pressure in the reactor at any time minus vapor pressure, MPa

P_0 = initial pressure in the reactor minus vapor pressure, MPa

R = gas constant, $\text{MPa m}^3 \text{kmol}^{-1} \text{K}^{-1}$

T = temperature of the gas in the reactor, K

V_L = liquid volume in the reactor, m^3

V_G = void space in the reactor, m^3

Z = compressibility factor

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